

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
14 December 2000 (14.12.2000)

PCT

(10) International Publication Number
WO 00/74823 A1

(51) International Patent Classification⁷: **B01D 53/94,**
F01N 3/021, 3/023, 3/08, 3/10, 3/20

James [GB/GB]; 9 Greenacres, Duxford, Cambridge CB2
4RB (GB). TWIGG, Martyn, Vincent [GB/GB]; 108 Er-
mine Street, Caxton, Cambridge CB3 8PQ (GB).

(21) International Application Number: PCT/GB00/02062

(22) International Filing Date: 30 May 2000 (30.05.2000)

(74) Agent: WISHART, Ian, Carmichael; Johnson Matthey
Technology Centre, Blounts Court, Sonning Common,
Reading RG4 9NH (GB).

(25) Filing Language: English

(26) Publication Language: English

(81) Designated States (*national*): CA, JP, US.

(30) Priority Data:
9913331.6 9 June 1999 (09.06.1999) GB

(84) Designated States (*regional*): European patent (AT, BE,
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,
NL, PT, SE).

(71) Applicant (*for all designated States except US*): JOHN-
SON MATTHEY PUBLIC LIMITED COMPANY
[GB/GB]; 2-4 Cockspur Street, Trafalgar Square, London
SW1Y 5BG (GB).

Published:

— With international search report.

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): BRISLEY, Robert,

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

(54) Title: TREATMENT OF EXHAUST GAS

(57) Abstract: A method of treating exhaust gas, especially from diesel engines producing low quantities of NO_x, comprises a first step in which HC is oxidised, producing CO₂ and H₂O, and a second step in which soot is combusted by reaction with NO₂. The method is characterised by the oxidation of ammonia (or a precursor thereof) to form NO_x, and the introduction of the thus formed NO_x into the exhaust gas before the performance of the second step.

WO 00/74823 A1

TREATMENT OF EXHAUST GAS

This invention relates to treatment of exhaust gas, in particular from internal combustion engines.

5

Certain types of such engines, especially lean-burn engines such as diesels, produce exhaust gas containing inter alia nitrogen oxides (NO_x) and combustible particulate (soot). The exhaust gases from lean-burn engines are net-oxidising, making the reduction of NO_x to N₂ more difficult than in a gasoline engine system where approximately equivalent amounts of oxygen and fuel are used. Removal of soot has been made practicable by the Johnson-Matthey Continuously Regenerating Trap ("CRT"TM) process (EP-A-0341832, US 4902487), in which soot is collected on a filter and oxidised by NO₂ that has been enriched in concentration by a preceding step of NO oxidation.

15 This process, however, is applicable only to exhaust containing, after the preceding oxidation step, at least enough NO₂ to oxidise the soot. If an engine is operated with low NO_x generation a technical problem arises. The low NO_x can result from engine design, expedients such as Exhaust Gas Recycle (EGR), temporary non-normal load or fuel or temperature conditions, deliberate less-lean engine operation or by injection of reductant
20 into the exhaust gas. The prior processes may convert NO_x to N₂ to a small extent, for example 3-8%. (Hawker et al. SAE paper 970182).

According to the invention a process for treating combustion exhaust gas containing HC, CO, O₂, soot and possibly NO_x that comprises the steps of:

- 25 i oxidising HC to CO₂ and H₂O, and NO (if present) to NO₂; and
ii oxidising said soot by reaction with NO₂:

is characterised by the step of generating NO_x by oxidising ammonia (as hereinafter defined) and introducing it into the exhaust gas upstream of step ii. Suitably soot is collected on a filter in step ii, but this is not presently regarded as essential if soot is
30 collected or adheres to the walls or front face of a catalytic component or has an extended residence time in the equipment.

Conveniently such ammonia oxidation is effected in step i, using therein one or more catalysts effective alone or together to promote oxidation of HC, CO, NO and ammonia.

Preferably HC and CO are oxidised in a first stage within step i and NO is oxidised to NO₂ with the fed ammonia in a second stage. (Such a divided step i is the subject of a co-pending GB application 99.13300.1, part of PCT application GB99/03971).

The term 'ammonia' in relation to added reactants includes also other compounds that produce NO_x in the oxidising reaction conditions. Thus for example amino- or amido-compounds can be used, for example hydrazine, urea, guanidine, biuret, cyanuric acid, lower alkylamines such as methylamines, and nitroxy compounds. Ammonia itself or any of these can be injected with other materials, such as: (where appropriate) a non-interfering acid such as carbonic acid; another fluid, suitably providing a liquid solution at ambient temperature that may be oxidisable; steam; air.

The introduction of NO_x ("first ammonia addition") may be continuous or intermittent.

Especially since the first ammonia addition increases the NO_x content of the gas to a level above that due to the engine, the process preferably includes also, after step ii, a step of NO_x removal. Several procedures are available for such NO_x removal. The procedures are suitably based on catalytic methods, absorption methods, or a combination of both. Continuous catalytic decomposition of NO_x to N₂ uses a lean-NO_x catalyst possibly with adjustment of gas composition to equivalence or rich, or with injection of a NO_x-specific reactant such as ammonia (using selective catalytic reduction, SCR). Absorption can be long-term (the absorber is eventually removed and regenerated) or short-term (the absorber is regenerated in-line). Regeneration can be achieved using temperature increase, or using the catalytic methods for decomposition of NO_x to N₂. The preferred method of NO_x removal is use of an absorbent that contains and/or is followed by a catalyst for the NO_x-reducing reaction. The addition of a NO_x-specific reactant and the use of SCR to regenerate the absorbent is especially preferred. The provision of NO_x specific reactant downstream of step ii will be referred to as "second ammonia addition".

The source of ammonia for the second addition can be selected from the sources specified for the first addition, except for compounds containing oxidisable carbon radicals or reducible nitrogen radicals, since the second addition is to react with NO_x to give N₂.

5 Whereas either ammonia addition can be continuous or intermittent, the intermittent/intermittent combination is preferred.

The first ammonia addition may be controlled to provide incomplete reaction or may be in excess, thereby slipping enough ammonia to provide the second ammonia addition.

10 The composition, temperature and flow-rate of engine exhaust commonly changes with time, for example when establishing steady conditions after start-up, or during changes in power output or chance variation. It is therefore desirable to control the exhaust treatment process to meet such changes. Intermittent first ammonia addition and the
15 resulting NO_x addition may be made in response to a signal from sensor means indicating that there is for example

- (i) inadequate NO_x content in the gas leaving the engine; or
- (ii) increase in soot filter pressure drop

20 which results because an engine has been operating for some time with inadequate NO_x or exhaust temperature too low to combust soot on the filter, so that a build-up of soot takes place. The NO_x addition is then made until the filter is substantially cleared.

25 If the oxidation of ammonia is effected over the step i catalyst, and if the engine is operated at varying levels of speed and/or load, such that the exhaust gas temperature varies, the first ammonia addition is made only when the temperature corresponds to formation of NO_x from ammonia preferentially to reaction of ammonia with NO_x. Since such intermittent ammonia produces an upward step in NO_x content, the second ammonia addition will normally coincide in time with it or follow very soon after it. Such addition is controlled in response to detection of NO_x exiting the absorber or to the (approaching) end
30 of a time period designed for the absorber. This programmed regeneration period typically lasts 1 to 100 seconds.

The temperatures of the gas at the various stages of the process are controlled as follows:

- (i) if the NO_x addition is made by oxidising ammonia in step i, the temperature is desirably over 200°C, for example in the range 350°- 500°C;
- (ii) for regeneration of a NO_x absorber, the temperature should be for example 150°-300°C. This is easier to achieve if the second ammonia addition is intermittent, since intermittently higher temperature may be available in high speed engine running or can be obtained for example by oxidation of intermittently provided hydrocarbon in step i or on a pre-catalyst, typically for a time period of the same order as that of the second ammonia addition.

The catalysts and (if used) absorbent are suitably supported on a ceramic or metal honeycomb, coated with a surface-area enlarging washcoat comprising one or more of alumina, zirconia, silicon carbide or other, generally oxidic, material. Coated on the washcoat, in one or more layers, is the active catalytic and/or absorptive material, to be described in more detail below. The honeycomb has typically 50-400 cells per square inch, possibly more, eg up to 1200. The range 200-900 is of general application.

In the oxidation catalyst the active material comprises generally a platinum group metal ("PGM"), especially platinum and/or palladium, optionally with other PGMs, eg rhodium, and other catalytic or promoting components. The exact composition and structure of the oxidation catalyst is not critical to operation of the invention, and hence may be varied according to the requirements of the situation. A low temperature light-off formulation is generally preferred. Conventional manufacturing techniques may be used.

The catalyst should of course be sized and composed to achieve the necessary conversions, and the design should minimise trapping of soot.

The filter may be any capable of trapping the soot without causing excessive back-pressure. In general, ceramic, sintered metal or woven or non-woven wire filters are usable, and wall-flow honeycomb structures may be particularly suitable. The structural material of the filter is preferably porous ceramic oxide, silicon carbide or sintered metal. A coating such as alumina, and also a catalyst such as La/Cs/V₂O₅ or PGM may be present. The soot

is generally carbon and/or heavy hydrocarbons, and is converted to carbon oxides and H₂O. Certain embodiments of this principle are described in the above-referenced patent documents, the teaching of which is incorporated herein by reference.

5 The absorbent may be selected from:

(a) compounds of alkali metals, alkaline earth metals, rare earth metals and transition metals, capable of forming nitrates and/or nitrites of adequate stability in absorbing conditions and of evolving nitrogen oxides and/or nitrogen in regenerating conditions;

10 (b) adsorptive materials such as zeolites, carbons and high-area oxides.

Compounds (a) may be present (before NO_x absorption) as composite oxides, eg of alkaline earth metal and copper such as Ba-Cu-O or MnO₂-BaCuO₂, possibly with added Ce oxide, or Y-Ba-Cu-O and Y-Sr-Co-O. (The oxides are referred to for simplicity, but in practice hydroxides, carbonates and nitrogen acid salts are present, depending on the temperature and gas composition).

15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
110
115
120
125
130
135
140
145
150
155
160
165
170
175
180
185
190
195
200
205
210
215
220
225
230
235
240
245
250
255
260
265
270
275
280
285
290
295
300
305
310
315
320
325
330
335
340
345
350
355
360
365
370
375
380
385
390
395
400
405
410
415
420
425
430
435
440
445
450
455
460
465
470
475
480
485
490
495
500
505
510
515
520
525
530
535
540
545
550
555
560
565
570
575
580
585
590
595
600
605
610
615
620
625
630
635
640
645
650
655
660
665
670
675
680
685
690
695
700
705
710
715
720
725
730
735
740
745
750
755
760
765
770
775
780
785
790
795
800
805
810
815
820
825
830
835
840
845
850
855
860
865
870
875
880
885
890
895
900
905
910
915
920
925
930
935
940
945
950
955
960
965
970
975
980
985
990
995
1000
1005
1010
1015
1020
1025
1030
1035
1040
1045
1050
1055
1060
1065
1070
1075
1080
1085
1090
1095
1100
1105
1110
1115
1120
1125
1130
1135
1140
1145
1150
1155
1160
1165
1170
1175
1180
1185
1190
1195
1200
1205
1210
1215
1220
1225
1230
1235
1240
1245
1250
1255
1260
1265
1270
1275
1280
1285
1290
1295
1300
1305
1310
1315
1320
1325
1330
1335
1340
1345
1350
1355
1360
1365
1370
1375
1380
1385
1390
1395
1400
1405
1410
1415
1420
1425
1430
1435
1440
1445
1450
1455
1460
1465
1470
1475
1480
1485
1490
1495
1500
1505
1510
1515
1520
1525
1530
1535
1540
1545
1550
1555
1560
1565
1570
1575
1580
1585
1590
1595
1600
1605
1610
1615
1620
1625
1630
1635
1640
1645
1650
1655
1660
1665
1670
1675
1680
1685
1690
1695
1700
1705
1710
1715
1720
1725
1730
1735
1740
1745
1750
1755
1760
1765
1770
1775
1780
1785
1790
1795
1800
1805
1810
1815
1820
1825
1830
1835
1840
1845
1850
1855
1860
1865
1870
1875
1880
1885
1890
1895
1900
1905
1910
1915
1920
1925
1930
1935
1940
1945
1950
1955
1960
1965
1970
1975
1980
1985
1990
1995
2000
2005
2010
2015
2020
2025
2030
2035
2040
2045
2050
2055
2060
2065
2070
2075
2080
2085
2090
2095
2100
2105
2110
2115
2120
2125
2130
2135
2140
2145
2150
2155
2160
2165
2170
2175
2180
2185
2190
2195
2200
2205
2210
2215
2220
2225
2230
2235
2240
2245
2250
2255
2260
2265
2270
2275
2280
2285
2290
2295
2300
2305
2310
2315
2320
2325
2330
2335
2340
2345
2350
2355
2360
2365
2370
2375
2380
2385
2390
2395
2400
2405
2410
2415
2420
2425
2430
2435
2440
2445
2450
2455
2460
2465
2470
2475
2480
2485
2490
2495
2500
2505
2510
2515
2520
2525
2530
2535
2540
2545
2550
2555
2560
2565
2570
2575
2580
2585
2590
2595
2600
2605
2610
2615
2620
2625
2630
2635
2640
2645
2650
2655
2660
2665
2670
2675
2680
2685
2690
2695
2700
2705
2710
2715
2720
2725
2730
2735
2740
2745
2750
2755
2760
2765
2770
2775
2780
2785
2790
2795
2800
2805
2810
2815
2820
2825
2830
2835
2840
2845
2850
2855
2860
2865
2870
2875
2880
2885
2890
2895
2900
2905
2910
2915
2920
2925
2930
2935
2940
2945
2950
2955
2960
2965
2970
2975
2980
2985
2990
2995
3000
3005
3010
3015
3020
3025
3030
3035
3040
3045
3050
3055
3060
3065
3070
3075
3080
3085
3090
3095
3100
3105
3110
3115
3120
3125
3130
3135
3140
3145
3150
3155
3160
3165
3170
3175
3180
3185
3190
3195
3200
3205
3210
3215
3220
3225
3230
3235
3240
3245
3250
3255
3260
3265
3270
3275
3280
3285
3290
3295
3300
3305
3310
3315
3320
3325
3330
3335
3340
3345
3350
3355
3360
3365
3370
3375
3380
3385
3390
3395
3400
3405
3410
3415
3420
3425
3430
3435
3440
3445
3450
3455
3460
3465
3470
3475
3480
3485
3490
3495
3500
3505
3510
3515
3520
3525
3530
3535
3540
3545
3550
3555
3560
3565
3570
3575
3580
3585
3590
3595
3600
3605
3610
3615
3620
3625
3630
3635
3640
3645
3650
3655
3660
3665
3670
3675
3680
3685
3690
3695
3700
3705
3710
3715
3720
3725
3730
3735
3740
3745
3750
3755
3760
3765
3770
3775
3780
3785
3790
3795
3800
3805
3810
3815
3820
3825
3830
3835
3840
3845
3850
3855
3860
3865
3870
3875
3880
3885
3890
3895
3900
3905
3910
3915
3920
3925
3930
3935
3940
3945
3950
3955
3960
3965
3970
3975
3980
3985
3990
3995
4000
4005
4010
4015
4020
4025
4030
4035
4040
4045
4050
4055
4060
4065
4070
4075
4080
4085
4090
4095
4100
4105
4110
4115
4120
4125
4130
4135
4140
4145
4150
4155
4160
4165
4170
4175
4180
4185
4190
4195
4200
4205
4210
4215
4220
4225
4230
4235
4240
4245
4250
4255
4260
4265
4270
4275
4280
4285
4290
4295
4300
4305
4310
4315
4320
4325
4330
4335
4340
4345
4350
4355
4360
4365
4370
4375
4380
4385
4390
4395
4400
4405
4410
4415
4420
4425
4430
4435
4440
4445
4450
4455
4460
4465
4470
4475
4480
4485
4490
4495
4500
4505
4510
4515
4520
4525
4530
4535
4540
4545
4550
4555
4560
4565
4570
4575
4580
4585
4590
4595
4600
4605
4610
4615
4620
4625
4630
4635
4640
4645
4650
4655
4660
4665
4670
4675
4680
4685
4690
4695
4700
4705
4710
4715
4720
4725
4730
4735
4740
4745
4750
4755
4760
4765
4770
4775
4780
4785
4790
4795
4800
4805
4810
4815
4820
4825
4830
4835
4840
4845
4850
4855
4860
4865
4870
4875
4880
4885
4890
4895
4900
4905
4910
4915
4920
4925
4930
4935
4940
4945
4950
4955
4960
4965
4970
4975
4980
4985
4990
4995
5000
5005
5010
5015
5020
5025
5030
5035
5040
5045
5050
5055
5060
5065
5070
5075
5080
5085
5090
5095
5100
5105
5110
5115
5120
5125
5130
5135
5140
5145
5150
5155
5160
5165
5170
5175
5180
5185
5190
5195
5200
5205
5210
5215
5220
5225
5230
5235
5240
5245
5250
5255
5260
5265
5270
5275
5280
5285
5290
5295
5300
5305
5310
5315
5320
5325
5330
5335
5340
5345
5350
5355
5360
5365
5370
5375
5380
5385
5390
5395
5400
5405
5410
5415
5420
5425
5430
5435
5440
5445
5450
5455
5460
5465
5470
5475
5480
5485
5490
5495
5500
5505
5510
5515
5520
5525
5530
5535
5540
5545
5550
5555
5560
5565
5570
5575
5580
5585
5590
5595
5600
5605
5610
5615
5620
5625
5630
5635
5640
5645
5650
5655
5660
5665
5670
5675
5680
5685
5690
5695
5700
5705
5710
5715
5720
5725
5730
5735
5740
5745
5750
5755
5760
5765
5770
5775
5780
5785
5790
5795
5800
5805
5810
5815
5820
5825
5830
5835
5840
5845
5850
5855
5860
5865
5870
5875
5880
5885
5890
5895
5900
5905
5910
5915
5920
5925
5930
5935
5940
5945
5950
5955
5960
5965
5970
5975
5980
5985
5990
5995
6000
6005
6010
6015
6020
6025
6030
6035
6040
6045
6050
6055
6060
6065
6070
6075
6080
6085
6090
6095
6100
6105
6110
6115
6120
6125
6130
6135
6140
6145
6150
6155
6160
6165
6170
6175
6180
6185
6190
6195
6200
6205
6210
6215
6220
6225
6230
6235
6240
6245
6250
6255
6260
6265
6270
6275
6280
6285
6290
6295
6300
6305
6310
6315
6320
6325
6330
6335
6340
6345
6350
6355
6360
6365
6370
6375
6380
6385
6390
6395
6400
6405
6410
6415
6420
6425
6430
6435
6440
6445
6450
6455
6460
6465
6470
6475
6480
6485
6490
6495
6500
6505
6510
6515
6520
6525
6530
6535
6540
6545
6550
6555
6560
6565
6570
6575
6580
6585
6590
6595
6600
6605
6610
6615
6620
6625
6630
6635
6640
6645
6650
6655
6660
6665
6670
6675
6680
6685
6690
6695
6700
6705
6710
6715
6720
6725
6730
6735
6740
6745
6750
6755
6760
6765
6770
6775
6780
6785
6790
6795
6800
6805
6810
6815
6820
6825
6830
6835
6840
6845
6850
6855
6860
6865
6870
6875
6880
6885
6890
6895
6900
6905
6910
6915
6920
6925
6930
6935
6940
6945
6950
6955
6960
6965
6970
6975
6980
6985
6990
6995
7000
7005
7010
7015
7020
7025
7030
7035
7040
7045
7050
7055
7060
7065
7070
7075
7080
7085
7090
7095
7100
7105
7110
7115
7120
7125
7130
7135
7140
7145
7150
7155
7160
7165
7170
7175
7180
7185
7190
7195
7200
7205
7210
7215
7220
7225
7230
7235
7240
7245
7250
7255
7260
7265
7270
7275
7280
7285
7290
7295
7300
7305
7310
7315
7320
7325
7330
7335
7340
7345
7350
7355
7360
7365
7370
7375
7380
7385
7390
7395
7400
7405
7410
7415
7420
7425
7430
7435
7440
7445
7450
7455
7460
7465
7470
7475
7480
7485
7490
7495
7500
7505
7510
7515
7520
7525
7530
7535
7540
7545
7550
7555
7560
7565
7570
7575
7580
7585
7590
7595
7600
7605
7610
7615
7620
7625
7630
7635
7640
7645
7650
7655
7660
7665
7670
7675
7680
7685
7690
7695
7700
7705
7710
7715
7720
7725
7730
7735
7740
7745
7750
7755
7760
7765
7770
7775
7780
7785
7790
7795
7800
7805
7810
7815
7820
7825
7830
7835
7840
7845
7850
7855
7860
7865
7870
7875
7880
7885
7890
7895
7900
7905
7910
7915
7920
7925
7930
7935
7940
7945
7950
7955
7960
7965
7970
7975
7980
7985
7990
7995
8000
8005
8010
8015
8020
8025
8030
8035
8040
8045
8050
8055
8060
8065
8070
8075
8080
8085
8090
8095
8100
8105
8110
8115
8120
8125
8130
8135
8140
8145
8150
8155
8160
8165
8170
8175
8180
8185
8190
8195
8200
8205
8210
8215
8220
8225
8230
8235
8240
8245
8250
8255
8260
8265
8270
8275
8280
8285
8290
8295
8300
8305
8310
8315
8320
8325
8330
8335
8340
8345
8350
8355
8360
8365
8370
8375
8380
8385
8390
8395
8400
8405
8410
8415
8420
8425
8430
8435
8440
8445
8450
8455
8460
8465
8470
8475
8480
8485
8490
8495
8500
8505
8510
8515
8520
8525
8530
8535
8540
8545
8550
8555
8560
8565
8570
8575
8580
8585
8590
8595
8600
8605
8610
8615
8620
8625
8630
8635
8640
8645
8650
8655
8660
8665
8670
8675
8680
8685
8690
8695
8700
8705
8710
8715
8720
8725
8730
8735
8740
8745
8750
8755
8760
8765
8770
8775
8780
8785
8790
8795
8800
8805
8810
8815
8820
8825
8830
8835
8840
8845
8850
8855
8860
8865
8870
8875
8880
8885
8890
8895
8900
8905
8910
8915
8920
8925
8930
8935
8940
8945
8950
8955
8960
8965
8970
8975
8980
8985
8990
8995
9000
9005
9010
9015
9020
9025
9030
9035
9040
9045
9050
9055
9060
9065
9070
9075
9080
9085
9090
9095
9100
9105
9110
9115
9120
9125
9130
9135
9140
9145
9150
9155
9160
9165
9170
9175
9180
9185
9190
9195
9200
9205
9210
9215
9220
9225
9230
9235
9240
9245
9250
9255
9260
9265
9270
9275
9280
9285
9290
9295
9300
9305
9310
9315
9320
9325
9330
9335
9340
9345
9350
9355
9360
9365
9370
9375
9380
9385
9390
9395
9400
9405
9410
9415
9420
9425
9430
9435
9440
9445
9450
9455
9460
9465
9470
9475
9480
9485
9490
9495
9500
9505
9510
9515
9520
9525
9530
9535
9540
9545
9550
9555
9560
9565
9570
9575
9580
9585
9590
9595
9600
9605
9610
9615
9620
9625
9630
9635
9640
9645
9650
9655
9660
9665
9670
9675
9680
9685
9690
9695
9700
9705
9710
9715
9720
9725
9730
9735
9740
9745
9750
9755
9760
9765
9770
9775
9780
9785
9790
9795
9800
9805
9810
9815
9820
9825
9830
9835
9840
9845
9850
9855
9860
9865
9870
9875
9880
9885
9890
9895
9900
9905
9910
9915
9920
9925
9930
9935
9940
9945
9950
9955
9960
9965
9970
9975
9980
9985
9990
9995
10000
10005
10010
10015
10020
10025
10030
10035
10040
10045
10050

intermittent supplies, so that the exothermic reaction keeps the external catalyst warm and ready for quick response.

The invention provides a system comprising apparatus integers corresponding to the process as herein defined; and, further, a diesel engine having such an exhaust treatment system. The engine may be for example a heavy duty engine to be used for a duty including idling periods and/or temporary rich running. Another example is a light duty engine, especially if fitted with EGR and/or intended for duty including idling periods. Whichever category of diesel engine is used, it is operated preferably with a fuel containing less than 50 ppm w/w of sulphur compounds, calculated as S. Examples of low-S fuels are 'Swedish Environmental Class I diesel' and 'City diesel'. If fuel of more than 50ppm S is used, the system should include a sulphate trap.

The invention, at least in preferred forms, provides a process, system or engine capable of operation in compliance with projections of European Stage IV, as published in Directive 98/69/EC.

One preferred form of the invention is illustrated by reference to the accompanying drawing, which is a flowsheet of the process and system.

Referring to the drawing, engine 10 is a 4-cylinder in-line diesel. Its exhaust manifold and pipe 12 are lagged and lead via path A or path B to mixing point 14. Path A is direct and is used if the temperature of the exhaust gas is high enough for efficient operation of subsequent stages. Path B, to be used if the gas temperature needs to be increased, leads to oxidation pre-catalyst 13, on which hydrocarbons and CO react with O₂ to provide an exotherm. Hydrocarbons reacting on catalyst 13 may be present as a result of incomplete combustion in normal engine operation or may be provided or supplemented by injection ahead of catalyst 13 or by temporary less-lean operation of the engine. At point 14 ammonia gas may be injected. The gas then passes to oxidation catalyst 16, comprising platinum on alumina on a ceramic honeycomb having 400 cells per square inch. The outlet of catalyst 16 is connected to the inlet of soot filter 18, which comprises a ceramic honeycomb having porous internal walls permeable to gas but not to the soot. In 18 the soot undergoes

combustion by reaction with NO₂ formed in 16. The outlet from 18 leads to mixing point 20 at which ammonia gas may be injected, and thence to reactor 22, which provides alternatively:

(a) selective catalytic NO_x removal (SCR); or

(b) NO_x absorption combined with and/or followed by NO_x reduction catalyst.

In either event the catalyst and absorbent are supported on a washcoated honeycomb structure similar to that used in 16. The outlet of 22 is into tailpipe 24 and thence to atmosphere.

Ammonia is taken from external supply 26 and fed as required to mixing points 14 and 20 via valves 28 and 30 respectively. Valves 28 and 30 are under the control of a computer shown generally by 32. Computer 32 receives gas composition data and temperature data from sensors (not shown) just upstream of point 14 and is programmed to operate the actuator of valve 28 to open when the NO_x level in the gas is too low to combust the soot in filter 18 and when the temperature is correct for oxidation of ammonia to NO_x. It may also respond to: tail pipe gas composition, to ensure that the final gas does not contain unreacted ammonia or too much NO_x; and/or to pressure-drop across filter 18, to give warning of incomplete soot combustion.

If path B and catalyst 13 are used, computer 32 also receives gas temperature data from a sensor (not shown) just upstream of point 14 and is programmed to inject hydrocarbon at the inlet of catalyst 13 or to adjust the engine inlet air/fuel ratio to provide such hydrocarbon.

Among the modes of operation of the invention the following are particularly envisaged:

1. In steady engine running a feed of ammonia to point 14 is maintained continuously, giving sufficient NO_x and (from 16) sufficient NO₂ to combust the soot collecting in 18. At the same time a feed of ammonia to point 20 is maintained continuously and reacts with NO_x in the gas leaving filter 18 over SCR catalyst 22, to give N₂.

2. The feed of ammonia to point 14 is the same as in mode 1 or can be varied to meet changes in operating conditions. However, reactor 22 now contains a NO_x absorbent

followed by an SCR catalyst. Since NOx in the gas leaving filter 18 is now absorbed in 22, feed of ammonia to point 20 is withheld until the NOx absorbent is well charged, set going until the absorbent is regenerated, then withheld again. Mode 2 has an advantage over mode 1 that the reaction of NOx with ammonia takes place at a higher concentration of reactants.

- 5 It also provides a margin of safety for an engine operated with varying speeds and loads.

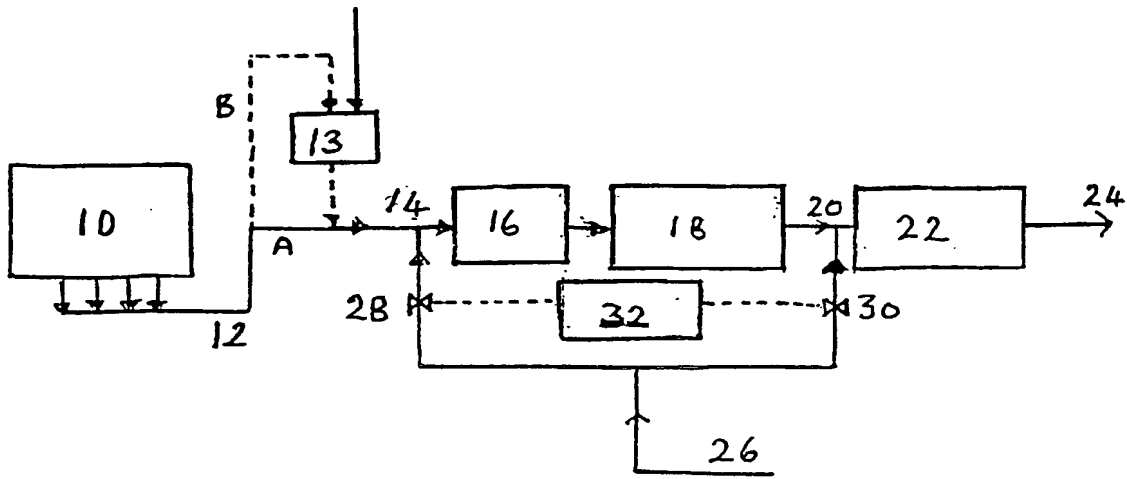
CLAIMS

1. Process for treating combustion exhaust gas containing HC, CO, O₂, soot and
5 possibly NO_x by the steps of
i oxidising HC to CO₂ and H₂O and (if present) NO to NO₂; and
ii oxidising said soot by reaction with NO₂:
characterised by the step of generating NO_x by oxidising ammonia (as hereinbefore
defined) and introducing it into the exhaust gas upstream of step ii.
- 10 2. Process according to claim 1 in which ammonia oxidation is effected in step i.
3. Process according to claim 1 or claim 2 in which HC and CO are oxidised in a first
stage within step i and NO is oxidised to NO₂ in a second stage.
- 15 4. Process according to claim 3 in which ammonia oxidation is effected in the second
stage of step i.
5. Process according to any one of the preceding claims including after step ii a step of
20 NO_x removal.
6. Process according to claim 5 comprising short-term absorption of NO_x, with
intermittent in-line regeneration by injection of NO_x-specific reactant such as
ammonia and reaction over an SCR catalyst, the catalyst being present in and/or
25 following the absorbent.
7. Process according to claim 6 in which ammonia oxidation is controlled to provide
incomplete reaction, thereby slipping enough ammonia to provide the NO_x-specific
reactant.
- 30 8. Process according to any one of the preceding claims in which said introduction of
NO_x is controlled in response to a signal from sensor means indicating that, in the

gas entering step i, the content of NO_x is or has become too low and/or the content of soot is or has become too high, relative to oxidation of soot by NO₂ in step ii.

- 5 9. Process according to claim 8 in which said injection of NO_x-specific reactant is controlled in response to:
- (a) tail pipe gas composition sensor indication of NO_x or ammonia in excess of design; and
- (b) if a NO_x absorber is used, programmed regeneration period.
- 10 10. Process according to any one of the preceding claims in which the step i catalyst is a supported platinum group metal.
11. Process according to any one of the preceding claims in which soot is collected on a filter.
- 15 12. Process according to any one of the preceding claims in which steps i and ii are carried out in a "CRTTM," system.
- 20 13. Process according to any one of the preceding claims in which the exhaust gas is the product of an engine operated with a fuel containing less than 50ppm w/w sulphur compounds calculated as S.
14. System comprising apparatus features corresponding to any one of claims 1 to 13.
- 25 15. A diesel engine having an exhaust treatment system according to claim 14.

1/1



INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/02062

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01D53/94 F01N3/021 F01N3/023 F01N3/08 F01N3/10
F01N3/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 00 21647 A (JOHNSON MATTHEY PUBLIC LIMITED COMPANY) 20 April 2000 (2000-04-20) page 1, line 5 -page 8, line 17; example 3 ---	1,2,5-7, 10-15
P,X	WO 00 21646 A (JOHNSON MATTHEY PUBLIC LIMITED COMPANY) 20 April 2000 (2000-04-20) page 2, line 10 -page 4, line 26 ---	1,2,5, 11,14,15
A	EP 0 758 713 A (TOYOTA JIDOSHA KABUSHIKI KAISHA) 19 February 1997 (1997-02-19) column 2, line 34 -column 8, line 20 ----- -/--	1,5,6, 10-12, 14,15

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

26 July 2000

Date of mailing of the international search report

02/08/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo.nl,
Fax: (+31-70) 340-3016

Authorized officer

Doolan, G

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/02062

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 835 684 A (JOHNSON MATTHEY PUBLIC COMPANY LIMITED) 15 April 1998 (1998-04-15) column 1, line 28 -column 5, line 11 -----</p>	<p>1,5, 10-15</p>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 00/02062

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 0021647	A	20-04-2000	AU	6111799 A	01-05-2000
WO 0021646	A	20-04-2000	AU	6100699 A	01-05-2000
EP 758713	A	19-02-1997	JP	9053442 A	25-02-1997
			US	5746989 A	05-05-1998
EP 835684	A	15-04-1998	JP	10159552 A	16-06-1998
			NO	974706 A	14-04-1998

THIS PAGE BLANK (USPTO)